

A Microscopic Model of Gemini Surfactants:

Self-assemblies in Water and at Air-Water Interface

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We report the results of large scale Monte Carlo (MC) simulations of novel microscopic models of gemini surfactants to elucidate (i) their spontaneous aggregation in bulk water and (ii) their spatial organization in a system where water is separated from the air above it by a sharp well defined interface. We study the variation of the critical micellar concentration (CMC) with the variation of the (a) length of the spacer, (b) length of the hydrophobic tail and (c) the bending rigidity of the hydrocarbon chains forming the spacer and the tail; some of the trends of variation are counter-intuitive but are in excellent agreement with the available experimental results. Our simulations elucidate the effects of the geometrical shape, size and density of the surfactant molecules, the ionic nature of the heads and hydrophobicity/hydrophilicity of the spacer not only on the shapes of the micellar aggregates and the magnitude of the CMC, but also on their conformations close to the air-water interface.

Running title: Self-assemblies of gemini surfactants

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I. INTRODUCTION:

Soap molecules are common examples of surfactant molecules; these not only find wide ranging applications in detergent and pharmaceutical industries, food technology, petroleum recovery etc. but are also one of the most important constituents of cells in living systems. Therefore, physics, chemistry, biology and technology meet at the frontier area of interdisciplinary research on association colloids formed by surfactants¹.

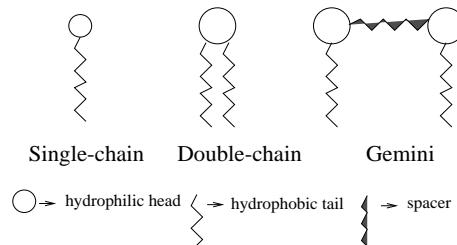


FIG. 1. Different types of amphiphiles.

The "head" part of surfactant molecules consist of a polar or ionic group. The "tail" of many surfactants consist of a single hydrocarbon chain whereas that of some other surfactants, e.g., phospholipids, are made of two hydrocarbon chains both of which are connected to the same head². In contrast, *gemini* surfactants^{3–6}, consist of two single-chain surfactants whose heads are connected by a "spacer" chain and, hence, these "double-headed" surfactants are sometimes also referred to as "dimeric surfactants"^{7,8} (see fig.1(a)). When put into an aqueous medium, the "heads" of the surfactants like to get immersed in water and, hence, are called "hydrophilic" while the tails tend to minimize contact with water and, hence, are called "hydrophobic"². The spacer in gemini surfactants is usually hydrophobic but gemini surfactants

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with hydrophilic spacers have also been synthesized⁹. Surfactant molecules are called "amphiphilic" because their heads are "water-loving" and hydrocarbon chains are "water-hating". Because of their amphiphilicity the surfactant molecules form "*self-assemblies*" (i.e., supramolecular aggregates), such as monolayer and bilayer membranes, micelles, inverted-micelles, etc.¹⁰, in a multi-component fluid mixture containing water.

In this paper we develop a microscopic model of *gemini* surfactants and, carrying out Monte Carlo (MC) computer simulations, investigate how the shapes and sizes of these molecules as well as their mutual interactions and their interactions with the molecules of water give rise to some unusual aggregation phenomena. Another aim of this paper is to report the results of a complimentary MC study of the spatial organization of these model gemini surfactants (particularly, their tails and spacers) at the air-water interface in order to answer some of the fundamental questions raised on this point and speculations made in the literature.

Micelles are formed when the concentration of the surfactants in water exceeds what is known as the critical micellar concentration (CMC)². In reality, CMC is not a single concentration (it is more appropriate to call it characteristic micellar concentration¹⁷). A longer hydrocarbon chain leads to larger area of contact between water and the hydrophobic part of an isolated surfactant molecule. Therefore, intuitively, one would expect that a longer hydrocarbon chain should enhance the tendency for aggregation, i.e., lower the CMC. This is, indeed, in agreement with the trend of variation of CMC of

single-chain surfactants with the length of the hydrophobic tail¹. In contrast, two unusual features of the CMC of gemini surfactants with *ionic heads* and *hydrophobic spacer* are:

- (i) for a given fixed length of each of the two tails, the CMC *increases* with the length of the spacer till it reaches a maximum beyond which CMC *decreases* with further increase of the spacer length^{7,11–13};
- (ii) for a given length of the spacer, the CMC *increases* with increasing tail length^{4,5}.

Moreover, the micellar aggregates formed by the gemini surfactants with short spacers even at low concentrations just above the CMC are "long, thread-like and entangled"^{8,14}, in contrast to the spherical shapes of the micelles formed by single-chain surfactants at such low concentrations. Furthermore, the CMC of gemini surfactants with *ionic heads* and *hydrophilic spacer* decrease monotonically with the increase of the length of the spacer²⁸. Our aim is to understand the physical origin of these unusual properties of gemini surfactants. We also make some new predictions on the morphology of the micellar aggregates of gemini surfactants with long tails and long spacer.

Synthesis of gemini surfactants with non-ionic (polar) heads in laboratory experiments remains one of the challenging open problems. But, our computer experiments on model gemini surfactants with non-ionic heads enable us to predict their morphologies and the variation of their CMC with the lengths of tails and spacers.

In the presence of the air-water interface, where do the tails and the spacer of an isolated gemini surfactant find

themselves- do they lie inside water or outside (i.e., in the air), do they get crowded close to the interface or do they spread out as far away from the interface as possible? How does the effective area of cross-section of an isolated gemini surfactant at the air-water interface vary with the increase of the length of the spacer when the spacer is (a) hydrophobic, (b) hydrophilic? How do the conformations of the gemini surfactants and spatial organizations of their tails and spacers vary with the increase of the density which gives rise to unavoidable interactions (both direct and entropic) among the surfactants. We try to answer these fundamental questions by carrying out computer experiments on a microscopic model that we propose here.

In this paper we simulate gemini surfactants with (a) hydrophobic spacers and also those with (b) hydrophilic spacers. For each of these two types of gemini surfactants we consider both ionic and non-ionic (but polar) hydrophilic heads.

A microscopic lattice model of double-chain surfactants (with a single head) in aqueous solution was developed by Bernardes¹⁵ by modifying the Larson model of single-chain surfactants^{16,17,19}. In this paper we propose a microscopic lattice model of gemini surfactants by extending Bernardes' model so as to incorporate two hydrophilic heads connected by a *hydrophobic spacer*. A summary of the important preliminary results for the gemini surfactants with *hydrophobic* spacers has been reported elsewhere. In this paper we not only give details but also report the corresponding results for gemini surfactants with *hydrophilic* spacers and study the effects of

a third component (an oil) on the novel morphology of the micellar aggregates formed by the gemini surfactants in water.

A microscopic model for single-chain surfactants at the air-water interface was developed earlier by one of us^{23,24} by appropriately modifying the Larson model^{16,17,19} of ternary microemulsions^{29,10}. In this paper we replace the single-chain surfactants in the model introduced in ref.²³ by the model gemini surfactants developed here, thereby getting the desired microscopic model of gemini surfactants at the air-water interface.

The model and the characteristic quantities of interest are defined in section 2. The results on the micellar aggregates, in bulk water, formed by the gemini surfactants with hydrophobic and hydrophilic spacers are reported in two subsections of section 3. The results of the investigations on the spatial organization of the gemini surfactants with hydrophobic and hydrophilic spacers at the air-water interface are given in section 4. Finally, a summary of the main results and the conclusions drawn from these are given in section 5.

II. THE MODEL AND THE CHARACTERISTIC QUANTITIES OF INTEREST:

A. General aspects

The Larson model was originally developed for ternary microemulsions which consist of water, oil and surfactants. In the spirit of lattice gas models, the fluid under investigation is modelled as a simple cubic lattice of size $L_x \times L_y \times L_z$. Each of the molecules of water (and oil) can occupy a single lattice site. A surfactant occupies several

lattice sites each successive pairs of which are connected by a rigid nearest-neighbour bond. A single-chain surfactant can be described by the symbol ¹⁹ $\mathcal{T}_m \mathcal{N}_p \mathcal{H}_q$ where \mathcal{T} denotes *tail*, \mathcal{H} denotes *head* and \mathcal{N} denotes the 'liason' or neutral part of the surfactants. m , p and q are integers denoting the lengths of the tail, neutral region and head, respectively, in the units of lattice sites. Thus, each single-chain surfactant is a self-avoiding chain of length $\ell = (m + p + q)$. We shall refer to each site on the surfactants as a *monomer*. The "water-loving" head group is assumed to be "water-like" and, similarly, the "oil-loving" tail group is assumed to be "oil-like".

Jan, Stauffer and collaborators¹⁷ simplified the Larson model by formulating it in terms of Ising-like variables which interact with nearest-neighbour interaction J , in the same spirit in which a large number of simpler lattice models had been formulated earlier²⁰ for the convenience of calculations. In this reformulation, a classical Ising spin variable S is assigned to each lattice site; $S_i = 1$ (-1) if the i -th lattice site is occupied by a water (oil) molecule. If the j -th site is occupied by a monomer belonging to a surfactant then $S_j = 1, -1, 0$ depending on whether the monomer at the j th site belongs to head, tail or neutral part. The monomer-monomer interactions are taken into account through the interaction between the corresponding pair of Ising spins which is assumed to be non-zero provided the spins are located on the nearest-neighbour sites on the lattice. Thus, the Hamiltonian for the system is given by the standard form

$$H = -J \sum_{\langle ij \rangle} S_i S_j. \quad (1)$$

where attractive interaction (analogue of the ferromagnetic interaction in Ising magnets) corresponds to $J > 0$ and repulsive interaction (analogue of antiferromagnetic interaction) corresponds to $J < 0$ ¹⁷. The temperature T of the system is measured in the units of J/k_B where k_B is the Boltzmann constant.

Jan, Stauffer and collaborators¹⁷ extended the model further to describe single-chain surfactants with ionic heads. According to their formulation, the monomers belonging to the ionic heads have Ising spin $+2$ to mimic the presence of electric charge. The repulsive interaction between a pair of ionic heads is taken into account through an (antiferromagnetic) interaction $J = -1$ between pairs of nearest neighbour sites both of which carry spins $+2$; however, the interaction between all other pairs of nearest-neighbour spins is assumed to be $J = 1$. By restricting the range of the repulsive (antiferromagnetic) interaction between the "charged" heads to only one lattice spacing one is, effectively, assuming very strong screening of the Coulomb repulsion between ionic heads by the counterions.

Note that the monomers of the same surfactant as well as different surfactants are not allowed to occupy the same lattice site simultaneously; this represents a hard-core intra-chain as well as inter-chain repulsion for monomer separations smaller than one lattice spacing. Moreover, at any non-vanishing temperature, during the out-of-line thermal fluctuations of the chains, the hard-core repulsion leads to steric repulsion between the chains. Some interesting consequences of steric repulsions between single-chain surfactants have been ob-

served in earlier MC studies^{23–25}. To our knowledge, no potential energies associated with the torsion of the surfactant chains have been incorporated so far in any work on Larson-type models.

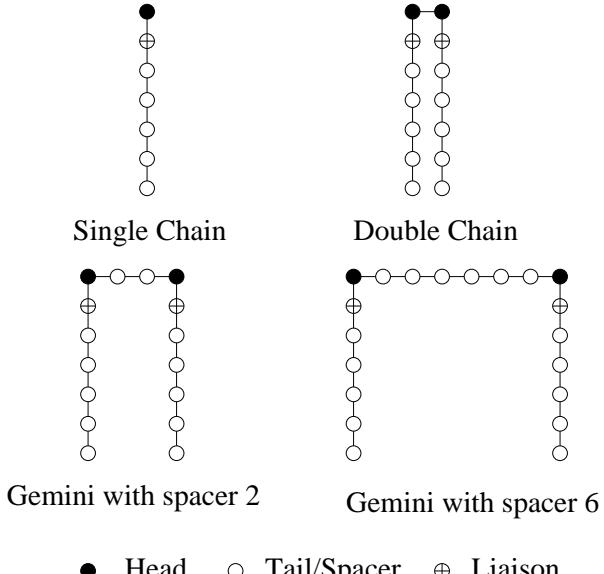


FIG. 2. Larson-type models of single-chain, double-chain and gemini surfactants.

Now we propose a microscopic lattice model of gemini surfactants. In terms of the symbols used above to denote the primary "structure" of the microscopic lattice model of single-chain surfactants, Bernardes' lattice model of double-chain surfactants, with a single hydrophilic head, can be described by the symbol $T_m \mathcal{N}_p \mathcal{H}_q \mathcal{N}_p T_m$. In terms of the same symbols, the microscopic lattice model of a gemini surfactant, which we propose here, can be represented by the symbol $T_m \mathcal{N}_p \mathcal{H}_q \mathcal{S}_n \mathcal{H}_q \mathcal{N}_p T_m$ where n is the number of lattice sites constituting the spacer represented by the symbol \mathcal{S} (see fig.1(b)).

Next, for the convenience of computation, we formulate the model in terms of classical Ising spin variables, generalizing the corresponding formulation for the single-chain surfactants reported in ref¹⁷. To our knowledge,

all the gemini surfactants synthesized so far have ionic heads. Therefore, we incorporate the effects of the ionic heads following ref¹⁷; if the j -th site is occupied by a monomer belonging to a surfactant then $S_j = 1, -1, 0$ depending on whether the monomer at the j th site belongs to hydrophilic spacer, tail (or, hydrophobic spacer), neutral part, respectively while $S_j = +2$ if the j -th site is occupied by an ionic head. The monomer-monomer interactions are taken into account through the interaction between the corresponding pair of Ising spins the Hamiltonian for which is given by equation (1).

In order to predict the properties of gemini surfactants with non-ionic (polar) heads and to investigate which of the aggregation phenomena exhibited by the ionic gemini surfactants arise from the electric charge on their ionic heads, we have also considered a model of gemini surfactants with non-ionic polar heads which is obtained from the model of ionic gemini surfactants by replacing all the $+2$ Ising spin variables by Ising spin $+1$ (and, accordingly, the interactions -1 between the heads on nearest-neighbour sites are replaced by $+1$). Moreover, in order to investigate the role of the chain stiffness we have used a chain bending energy²⁴; every bend of a tail or a spacer, by a right angle at a lattice site, is assumed to cost an extra amount of energy $K(> 0)$.

Starting from an initial state (which will be described in the subsections 2.1 and 2.2), the system is allowed to evolve following the standard Metropolis algorithm: each of the attempts to move a surfactant takes place certainly if $\Delta E < 0$ and with a probability proportional to $\exp(-\Delta E/T)$ if $\Delta E \geq 0$, where ΔE is the change in

energy that would be caused by the proposed move of the surfactant under consideration.

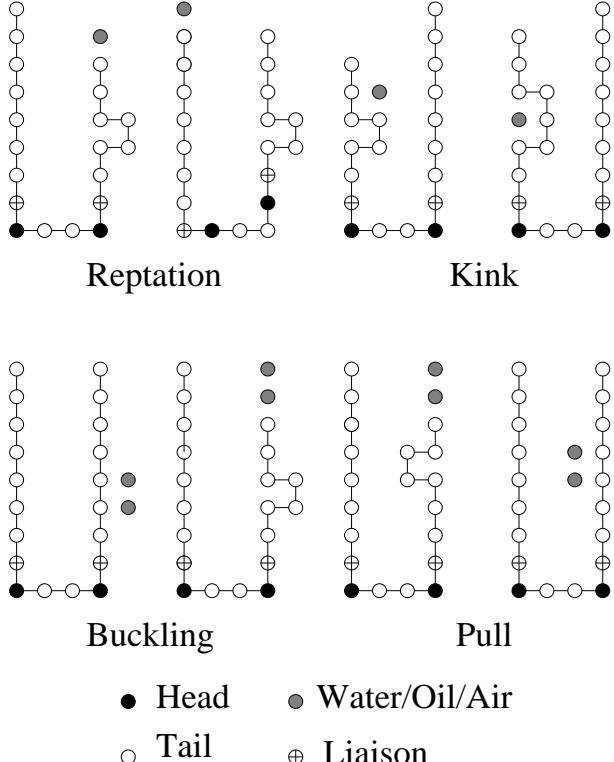


FIG. 3. Schematic representation of the moves attempted by every surfactant at every MC step.

Next, we specify the allowed moves of the surfactants for the appropriate sampling of the states of the system in a MC simulation. So far as the single-chain surfactants are concerned, the only move which was allowed in the pioneering works is

reptation: one of the two ends of each surfactant is picked up randomly, with equal probability, and the surfactant is allowed to move forward along its own contour by one lattice spacing with the probability mentioned above; this move effectively mimics the reptile-like slithering of the surfactants and hence the name. Subsequently, several new moves have been introduced in order to speed up the process of equilibration¹⁹. We have generalized

these moves appropriately for the gemini surfactants and schematic representation of these moves are shown in fig.2; although the moves are illustrated using one of two tails, each of the moves (except reptation, which involves the entire surfactant) in our algorithm is equally likely to be applied on the two tails as well as the spacer. The moves allowed for the surfactants in our model are as follows:

(i) *reptation*: this is identical to the reptation move for single-chain surfactants described above; (ii) *spontaneous chain buckling*: a portion in the middle of one of the two tails or the spacer is randomly picked up and allowed to buckle with the probability mentioned above; (iii) *kink movement*: a kink formed by the buckling or reptation is allowed to move to a new position with the appropriate probability calculated according to the prescription mentioned above; (iv) *pull move*: this is the reverse of spontaneous chain buckling; a buckled part of one of the two tails or the spacer is pulled so as to make it more extended. In addition to these moves, each of the surfactants is allowed to move laterally in one of the six possible directions, which is chosen randomly with probability 1/6, and each monomer of the surfactant is moved in that direction by one lattice spacing. each of these moves is possible only if the new positions of all the monomers are not occupied simultaneously by monomers belonging to other surfactants. Each surfactant is allowed to try each of the above mentioned moves once during each MC step. The moves of the molecules of water and air are described in the subsections 2.1 and 2.2 below.

In principle, one can study the aggregation of gemini

surfactants deep inside bulk water and their spatial organization close to air-water interface by MC simulation of a single system where the lower part of the lattice representing water is sufficiently large and the density of surfactants is also sufficiently high so that a large fraction of these can be found deep inside water in the form of micellar aggregates. However, for the convenience of computation, we study these two aspects of the problem separately; in the first part we investigate only the phenomenon of aggregation of gemini surfactants in bulk water and in the second part we investigate only the spatial organization of the tails and spacers of the gemini surfactants at (and near) the air-water interface when the total volume fraction occupied by the surfactants is quite small. Both these parts of our computations are based on the general model described above and the specific differences involved in these two are explained separately in the next two subsections.

B. Model of Gemini Surfactants in Bulk Water:

In order to investigate the spontaneous formation of micellar aggregates and their morphology, model gemini surfactants are initially dispersed randomly in a $L_x \times L_y \times L_z$ system which contains only water and surfactants. Periodic boundary condition is applied in all the three directions thereby mimicking bulk water which is infinite in all the directions. So far as the moves of the molecules of water are concerned, each molecule of water is allowed to exchange position with a monomer belonging to a surfactant, provided that is necessary for the implementation of an attempted move of a surfactant.

C. Model of Gemini Surfactants at Air-Water Interface:

Just as in the preceeding subsection, the system under investigation is modelled as a simple cubic lattice of size $L_x \times L_y \times L_z$. However, in contrast to simulating a bulk of water, which is infinite in all directions, we now simulate a semi-infinite vertical column of air separated from a semi-infinite vertical column of water below by a sharp horizontal air-water interface. In the cartesian coordinate system we choose, the horizontal air-water interface is parallel to the XY -plane and the *vertically downward* direction is chosen as the $+Z$ -axis. Each of the molecules of water and air can occupy a single lattice site. A classical Ising spin variable S is assigned to each lattice site; $S_i = 1$ (-1) if the i -th lattice site is occupied by a water molecule (air molecule or empty). Our prescription for assigning the Ising spin variables to the sites occupied by the monomers of the amphiphiles is identical to that given in the preceeding subsection. Periodic boundary conditions are applied along the X and Y directions. The lattice sites in the uppermost and lowermost layers are occupied by "down" and "up" spins, respectively, which were not updated during the computer simulation. These boundary conditions mimic the physical situation, mentioned above, which we intend to simulate.

In the initial state the surfactants are so arranged that their spacers lie flat, and fully extended, horizontally in the first layer of water immediately below the air-water interface and their tails are fully extended vertically into air. The system is then allowed to evolve towards equilibrium following the Metropolis algorithm explained ear-

lier. So far as the moves of the individual molecules are concerned, air and water are not allowed to exchange positions, as dispersion of air and water inside each other is not possible in our model. However, if some monomers of a surfactant come out of water the vacant sites are occupied by inserting water molecules; this is consistent with our assumption that the water column is semi-infinite in the Z -direction. Moreover, we impose an additional constraint that none of the heads of the surfactant molecules can come out of water.

D. Characteristic Quantities of Interest:

The most direct approach to investigate the morphology of the micellar aggregates and the spatial organization of the different parts of individual surfactants is to look at the snapshots of the system after equilibration. For studying the variations of CMC with the lengths of the tails and spacers one has to use a well-defined prescription for computing the CMC; this is a subtle point as the CMC is not a unique single concentration, as mentioned before. We follow the prescription proposed, and used successfully in the case of single-chain surfactants¹⁷; we identify CMC as the amphiphile concentration where half of the surfactants are in the form of isolated chains and the other half in the form of clusters consisting of more than one neighbouring amphiphile.

We have introduced a quantitative measure of the effective cross-sectional area A of the gemini surfactants projected onto the air-water interface. We compute $|\Delta x|_m$ and $|\Delta y|_m$ which are the maximum differences in the X - and Y -coordinates, respectively, of the monomers and

define A as

$$A = [(|\Delta x|_m)^2 + (|\Delta y|_m)^2]^{1/2} \quad (2)$$

The vertical extension $\langle Z \rangle$ is defined as the difference in the Z - coordinates of the highest and lowest monomers (i.e. monomers with highest and lowest value of Z -coordinates) of a single surfactant²⁶. A quantitative measure of the gross features of the spatial organization of the tails and spacers of the gemini surfactants at the air-water interface is the equilibrium profiles of the concentrations of the corresponding monomers in the Z -direction, i.e., in the direction perpendicular to the air-water interface. More precisely, at each molecular layer, we count separately the *number* of monomers belonging to the tails and the spacers (and also the heads and neutral parts) in that particular layer and average the data over sufficiently large number of configurations after equilibration of the system.

We have carried out MC simulations of the model $T_m N_p H_q S_n H_q N_p T_m$ of gemini surfactants for $p = q = 1$ and for three different values of the tail length, namely, $m = 5, 15$ and 25 . In our simulation of the surfactants at the air-water interface we do not find any observable difference in the concentration profiles obtained in single runs for $100 \times 100 \times 100$ systems and for larger systems containing identical surface-density of surfactants, all the profiles reported in this paper have been generated for system sizes $L_x = L_y = L_z = L = 100$ by averaging over sufficiently large (10-25) number of runs. The same size of the system was also found to be large enough to avoid severe finite-size effects on the CMC data; each of the

data points for the CMC is obtained by averaging over typically 10 runs. For a given m we have computed the CMC for spacer lengths $2 \leq n \leq 20$.

III. MICELLAR AGGREGATES OF GEMINI SURFACTANTS:

A. Aggregates of Gemini Surfactants: Results for Hydrophobic Spacers

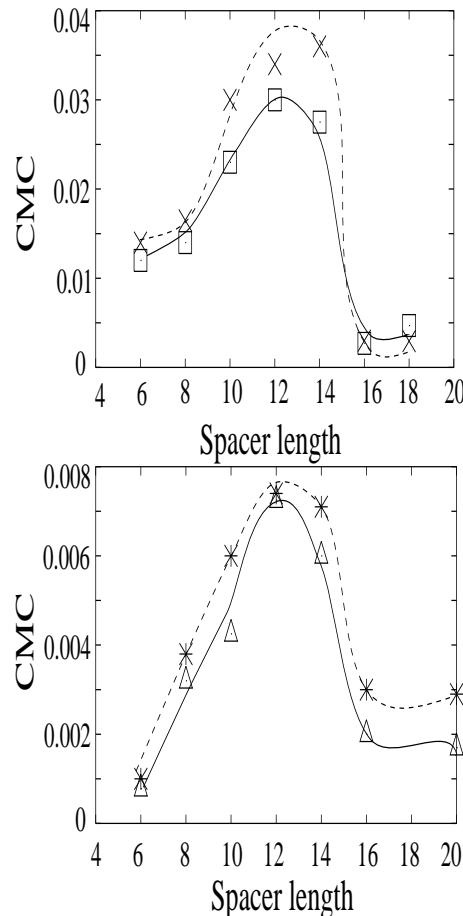


FIG. 4. (a)Variation of CMC of ionic geminis with hydrophobic spacer length; $m = 15$, $T = 2.2$. The symbols \square and \times correspond to $K = 0$ and $K = 2$, respectively. (b) Same as (a), except that $m = 5$. The symbols \triangle and $*$ correspond to $K = 0$ and $K = 2$, respectively. The continuous curves are merely guides to the eye.

The CMC of *ionic* gemini surfactants with *hydrophobic* spacers are plotted against the spacer length for two different lengths of the tail, namely, $m = 5$ and $m = 15$, in figs. 3 (a) and 3(b), respectively. The *non-monotonic*

variation of CMC with the spacer length, in figs. 3(a) and 3(b), is in qualitative agreement with the experimental observations^{11–14}. However, this is in sharp contrast to the monotonic decrease of the CMC with the length of the hydrophobic tail of single-chain model surfactants of the type $T_m\mathcal{N}_p\mathcal{H}_q$ ^{17,18}. Moreover, for a given length of the hydrophobic spacer, the CMC of this type of gemini surfactants *increases* when the bending stiffness K of the hydrophobic chains is switched on (see figs. 3(a) and (b)). Furthermore, we observe that, for a given length of the hydrophobic spacer, the CMC of ionic gemini surfactants *increase* with the increase of the tail length (see fig.4); this trend of variation is also consistent with the corresponding experimental observations^{4,5}.

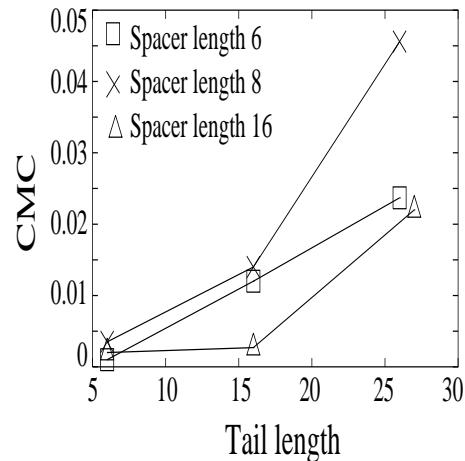


FIG. 5. Variation of CMC of ionic geminis with tail length at $T = 2.2$ for three different lengths of the hydrophobic spacer, namely, $n = 6, 8, 16$. The straight lines connecting the successive data points are merely guides to the eye.

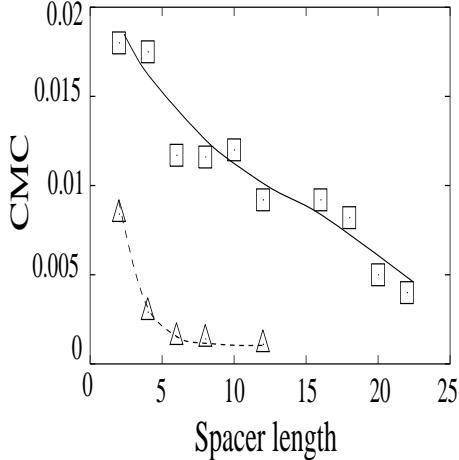


FIG. 6. Variation of CMC of non-ionic geminis with the length of the hydrophobic spacer; $m = 15$ (\square) and $m = 5$ (\triangle) both with $K = 0$ and at $T = 2.2$. The continuous curves are merely guides to the eye.

For a given tail length (see fig.5 for $m = 5$ and $m = 15$), the CMC of model gemini surfactants with *hydrophobic* spacers decreases *monotonically* with the increase in the spacer length when the polar head group is *non-ionic*. This is in sharp contrast to the non-monotonic variation observed for ionic gemini surfactants. However, for a given spacer length, the trend of the variation of CMC of non-ionic gemini surfactants with the tail length is similar to that observed for ionic gemini surfactants, i.e., CMC increases with the increase of the length of the tail.

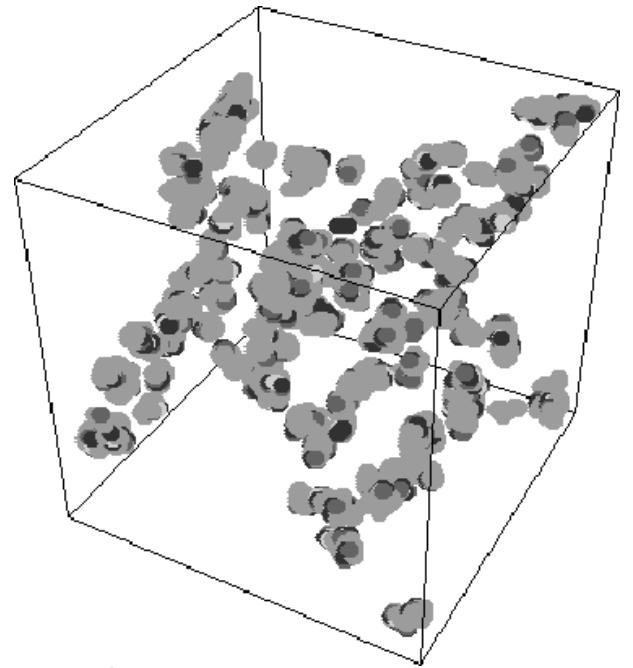


FIG. 7. Snapshots of the micellar aggregates formed by ionic geminis with hydrophobic spacer; $m = 15$, $n = 2$ and $K = 0$ at $T = 2.2$ when the surfactant density is 0.007. The symbols black spheres, dark grey spheres and light grey spheres represent monomers belonging to head, tail and spacer, respectively.

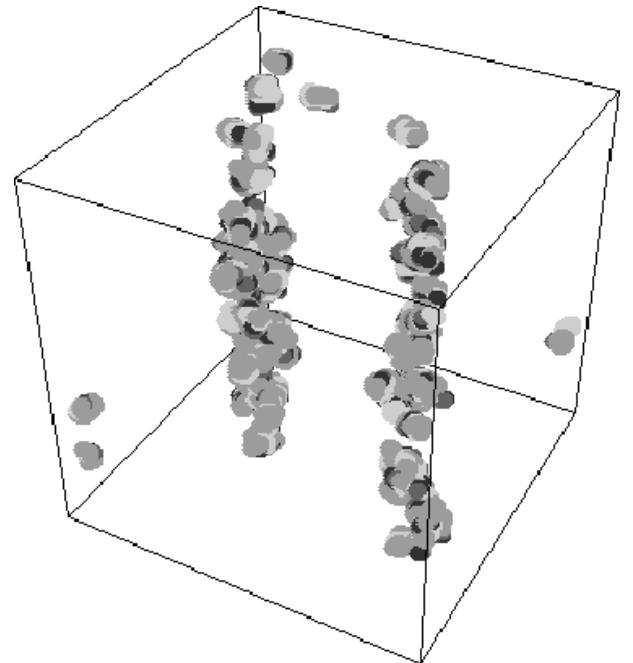


FIG. 8. Same as in fig. 6, except that $n = 16$ and the density is 0.005.

Instantaneous snapshots of the micellar aggregates formed by *long tailed* ($m = 15$) gemini surfactants with

ionic heads and *hydrophobic spacer* are shown for spacer lengths $n = 2$ (fig. 6) and $n = 16$ (fig.7). The morphology of the aggregates in fig.6 are similar to the "long, thread-like and entangled" micelles observed in laboratory experiments⁸ and in MD simulations²¹ on gemini surfactants with short hydrophobic spacers. Moreover, our data in fig.7 suggest that rod-like ("columnar") micelles are formed by gemini surfactants with *ionic head* and *long tail* ($m = 15$) when the length of the *hydrophobic spacer* is also long ($n = 16$). The morphologies of the aggregates in fig.6 and 7 are in sharp contrast with the spherical shape of the micelles (see fig.8) formed by single-chain ionic surfactants of comparable tail size even at concentrations somewhat higher than those in the figures 6 and 7.

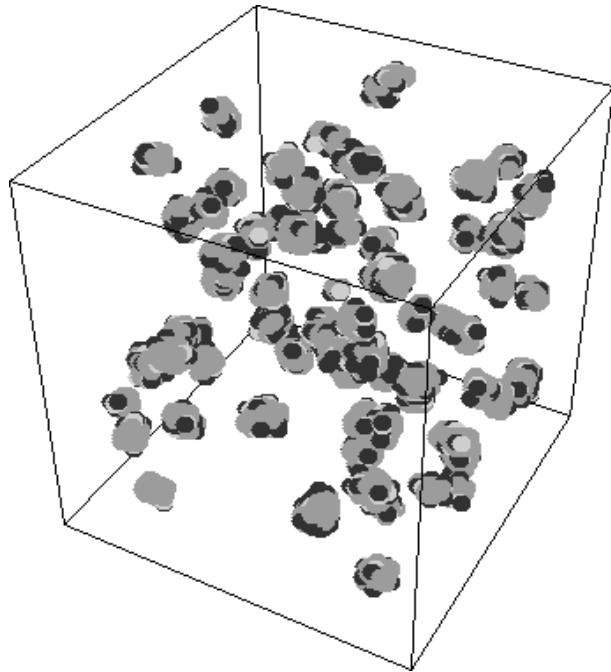


FIG. 9. Snapshots of micellar aggregates formed by single-chain ionic surfactants with $m = 14$ and the density 0.01. The symbols black spheres and grey spheres represent monomers belonging to head and tail, respectively.

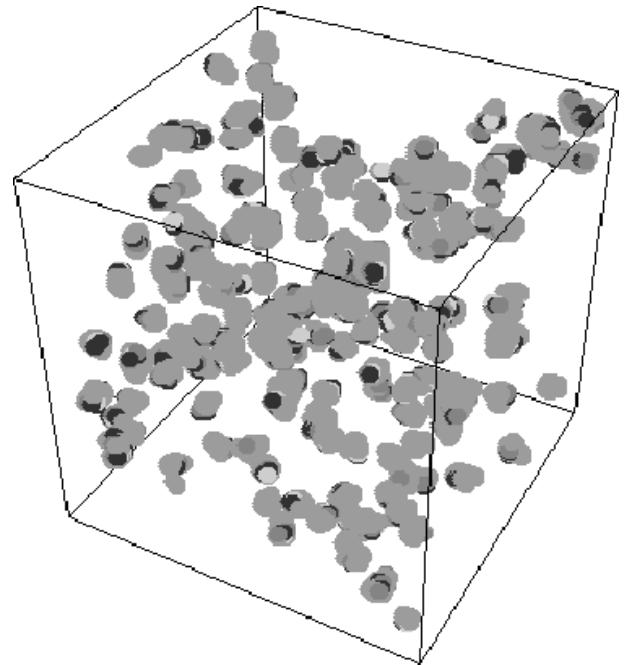


FIG. 10. Same as in fig. 6, except that the geminis are non-ionic.

There is no significant difference between the morphologies of the micellar aggregates of ionic and non-ionic single-chain model surfactants represented by the symbol $T_mN_pH_q$ ²². Similarly, we do not observe any significant difference also in the shapes of the aggregates of ionic surfactants (figs.6 and 7) and those of non-ionic gemini surfactants (see figs.9 and 10) with hydrophobic spacers, for given values of m , n and comparable concentration, in spite of qualitatively different trends of variation of their CMCs with spacer lengths.

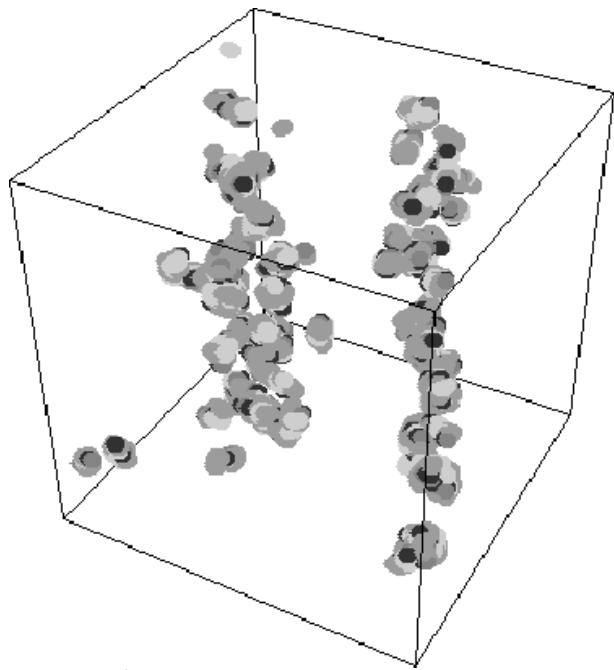


FIG. 11. Same as in fig. 7, except that the geminis are non-ionic.

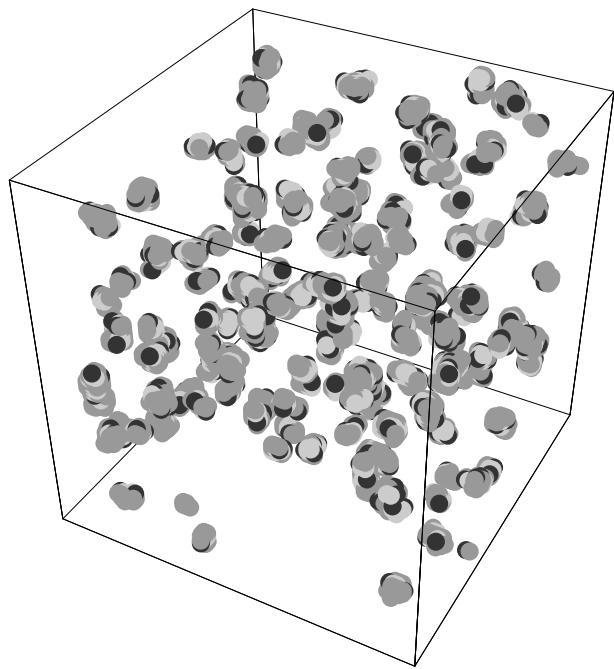


FIG. 12. Snapshots of micellar aggregates formed by ionic gemini surfactants with hydrophobic spacer; $m = 5$, $n = 6$ and $K = 0$ at $T = 2.2$ when the surfactant density is 0.005.

Note that the rod-like micelles, shown in fig.7, are formed when the length of the hydrophobic spacer and the combined length of the tail and the neutral part of the gemini surfactants are both equal to 16. Does this imply that rod-like micelles are formed whenever the hydrophobic spacer and the tail are equal (or comparable) in length? In order to answer this question we have also looked at the snapshots of the micellar aggregates of similar gemini surfactants with shorter tails and spacers; a typical example, shown in fig.11, corresponds to $m = 5$, $n = 6$. The fact that these micelles are also "long, thread-like and entangled", like those in fig.6, in contrast to the rod-like micelles of fig.7, suggests that the morphology of the ionic gemini surfactants with hydrophobic spacers is dominantly determined by the length of the spacer; long, thread-like micelles are formed if the spacer is short and rod-like micelles are formed if the spacer is long.

B. Aggregates of Gemini Surfactants; Results for Hydrophilic Spacers

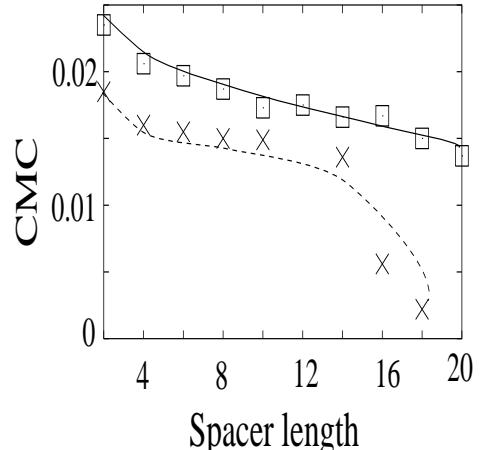


FIG. 13. (a) Variation of CMC of ionic geminis with hydrophilic spacer length; $m = 15$, $T = 2.2$. The symbols \square and \times correspond to $K = 0$ and $K = 2$, respectively.

In fig.12 we plot the CMC against the length of the *hydrophilic* spacer for gemini surfactants with *ionic* head and tail length $m = 15$ (the qualitative features of the corresponding curve for $m = 5$ are very similar and, therefore, not shown). In contrast to the non-monotonic variation of CMC observed earlier with the variation of the length of hydrophobic spacers, now we find a *monotonic* decrease of CMC with the increase of the length of the hydrophilic spacer. This trend of variation is in qualitative agreement with the corresponding experimental observation²⁸. Moreover, for given lengths of the hydrophobic spacer and the tail, n and m , the CMC for the bending energy $K = 2$ is lower than that for $K = 0$ (see fig.12); this trend of variation is exactly opposite to the corresponding trend observed earlier in the case of gemini surfactants with hydrophobic spacers.

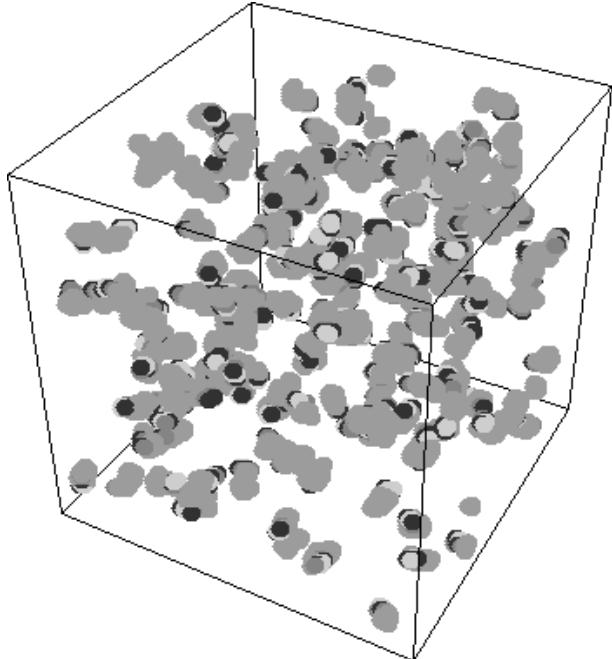


FIG. 14. Same as fig. 6 except that the spacer is hydrophilic.

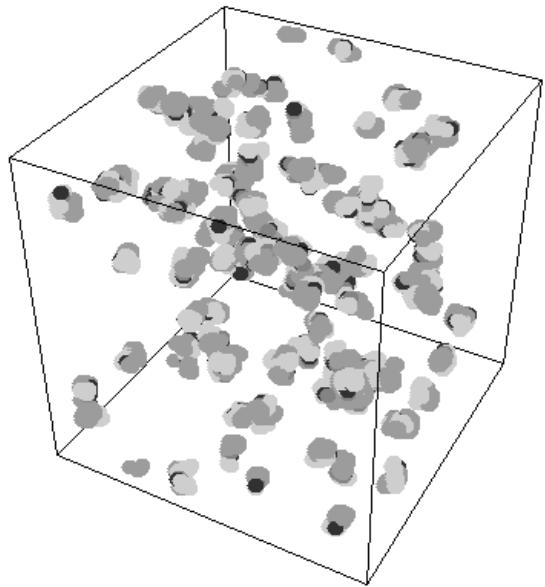


FIG. 15. Same as fig. 7 except that the spacer is hydrophilic.

The snapshots of the micellar aggregates formed by the gemini surfactants with *ionic heads* and *hydrophilic spacer* are shown for spacer lengths $n = 2$ (fig. 13) and for $n = 16$ (fig.14) for densities which are identical to those in the figs.6 and 7, respectively. Comparing the morphologies of the aggregates in fig.6 and fig.13 we find that the gemini surfactants with hydrophobic spacers form coarser (albeit fewer in number) aggregates compared to the corresponding geminis with hydrophilic spacers; this is also consistent with the fact that the CMC of the gemini surfactants with spacer length $n = 2$ are higher when the spacers are hydrophilic as compared to that for hydrophobic spacers.

The difference in the morphologies of ionic geminis with hydrophobic and hydrophilic spacers is much more striking when the spacer is longer ($n = 16$) (compare the fig.7 with fig.14)- the micelles are more or less spherical when the spacers are hydrophilic!

An important difference between the micellar aggre-

gates of gemini surfactants with hydrophobic spacers and those with hydrophilic spacers is that more spacer monomers are found on the outer surface of the aggregate (i.e., in contact with water) when the spacer is hydrophilic. This is consistent with one's intuitive expectation because the hydrophilic spacers like to be in contact with water.

The snapshots of the micellar aggregates of non-ionic gemini surfactants with hydrophilic spacers are very similar to those for the corresponding ionic gemini surfactants (and, therefore, not shown in any figure).

Hydrophilic spacers gain energy by remaining surrounded by water. On the other hand, hydrophobic spacers as well as tails try to avoid contact with water by hiding inside micellar aggregates. That is why in the snapshots of micellar aggregates we see that a larger number of monomers belonging to the spacers are in contact with water, when the spacers are hydrophilic, than those when the spacers are hydrophobic. And this is prominent particularly for long spacers.

IV. SPATIAL ORGANIZATION OF GEMINI SURFACTANTS AT AIR-WATER INTERFACE: RESULTS FOR HYDROPHOBIC AND HYDROPHILIC SPACERS

A. Dilute regime

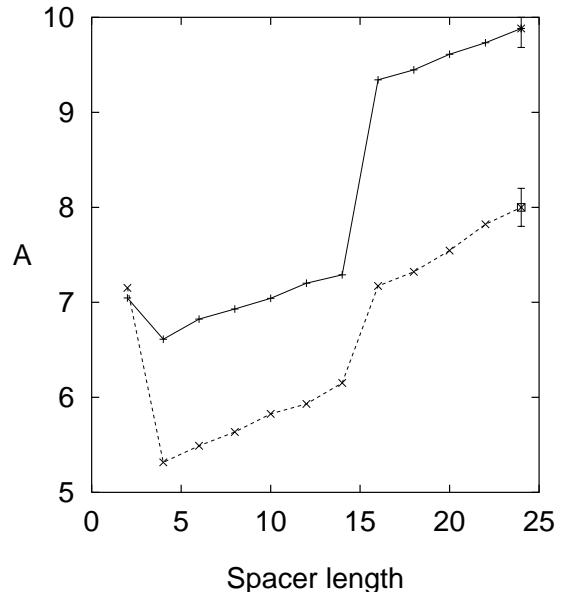


FIG. 16. Variation of cross-sectional area of isolated individual gemini surfactant with spacer spacer length. The solid line for hydrophobic spacer and broken line for hydrophilic spacer. To give an indication of the accuracy of the data points the error bar of only one point has been shown.

First let us consider the dilute regime where the concentration of the surfactants is so low that not only all of them remain, almost certainly, at the air-water interface but every surfactant may be regarded as, effectively, isolated from each other. In this limit the cross-sectional area A of the molecules is determined by only intramolecular interactions, which is dominated by the steric (entropic) interactions among the tails and the spacer. We plot the cross-sectional area A of isolated individual gemini surfactants as a function of the length of the spacer in fig.15, in both the cases of (a) hydrophobic and (b) hydrophilic spacers. The spacer is very stiff when its length is $n = 2$ as no wiggle can form. The area A for $n = 4$ is smaller than that for $n = 2$ irrespective of the

nature of the spacer (i.e., hydrophobic or hydrophilic); this is caused by the formation of wiggle on the spacer which brings the two heads closer. Further increase of the spacer length gives rise to a linear increase of the area A . However, a sharper increase in A takes place when the length of the spacer becomes equal to that of the tails; on both sides of this regime of sharp rise, the rate of increase of A with n is practically identical.

Because of its stiffness against wiggle formation, the spacer of length $n = 2$ can buckle neither towards air nor towards water and remains parallel (like a rigid rod) to the air-water interface. Therefore, if $n = 2$, the cross-sectional area A of isolated gemini surfactants with hydrophilic spacers is practically identical to that of gemini surfactants with hydrophobic spacers. However, for all larger values of n , A is smaller if the spacer is hydrophilic; a hydrophilic spacer buckles into water thereby leaving most of the space in the air above the heads available for occupation by the tails. On the other hand, the hydrophobic tails take up a substantial amount of available space in a cap-like volume in the air just above the heads thereby forcing the tails to spread out radially outward and, hence, increasing the effective area A .

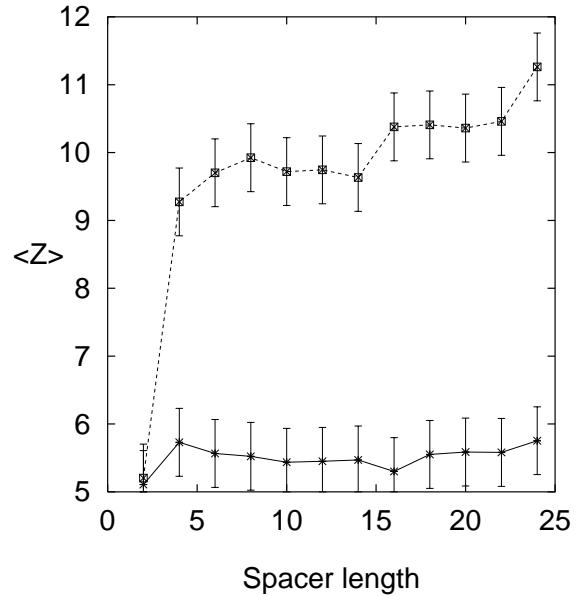


FIG. 17. Variation of vertical extension of individual gemini surfactant with spacer length. The solid line for hydrophobic spacer and broken line for hydrophilic spacer.

Evidence in support of this scenario emerges also from the plots of vertical extension V of the isolated gemini surfactants against the length of the spacer (see fig.16); a larger V of gemini surfactants with hydrophilic spacer, as compared to those of gemini surfactants with hydrophobic spacer of identical length, arises from the fact that the hydrophilic spacers buckle into water while their tails remain outside water.

B. High Surface Density regime

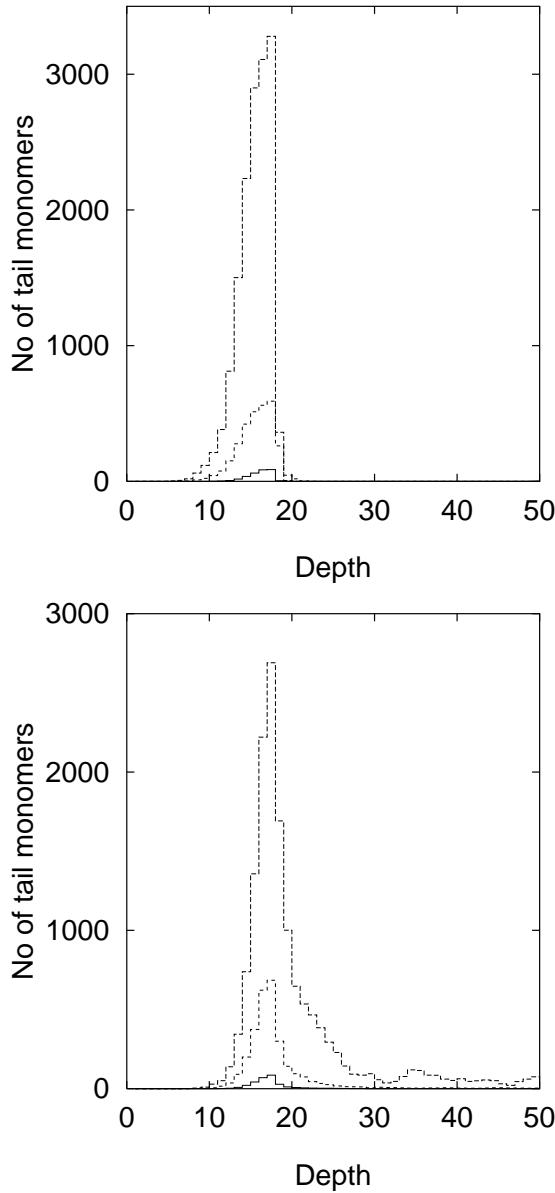


FIG. 18. Concentration profiles for tail monomers for three different cases when the number of amphiphiles present in the systems are (i) 500 (solid line), (ii) 100 (broken line) and (iii) 10 (dashed line).(a) hydrophobic spacer (b) hydrophilic spacer.

The concentration profiles of the tails of the gemini surfactants with hydrophobic spacers are shown in fig.17(a) and the corresponding concentration profiles for gemini surfactants with hydrophilic spacers are shown

in fig.17(b). In the case of gemini surfactants with hydrophobic spacer, the spacers minimize contact with water by arranging themselves just outside the water, but do not venture out too far from the interface. On the other hand, the hydrophilic spacers gain energy by moving inside water thereby leaving more space just outside water which become available for occupation by the tails; consequently, one would have naively expected, the tails of the gemini surfactants with hydrophilic spacers are likely to be found closer to the interface than those of the gemini surfactants with hydrophobic spacers. However, what we observe in reality in fig.17(b) is much more dramatic- a significantly large fraction of the monomers belonging to the tails are pulled into water along with the heads (see fig.18) to which they are attached! The loss of energy due to the increase in the area of contact between the hydrophobic tails and water is compensated by the gain of energy from the increase of contact between hydrophilic spacers and water as well as the gain of conformational entropy of the system arising from the larger amount of space available to those chains which remain at the interface. This interpretation is supported by our observation that this effect is more prominent at higher densities of surfactants. Some other manifestations of the entropic effect have been observed earlier^{23–25}.

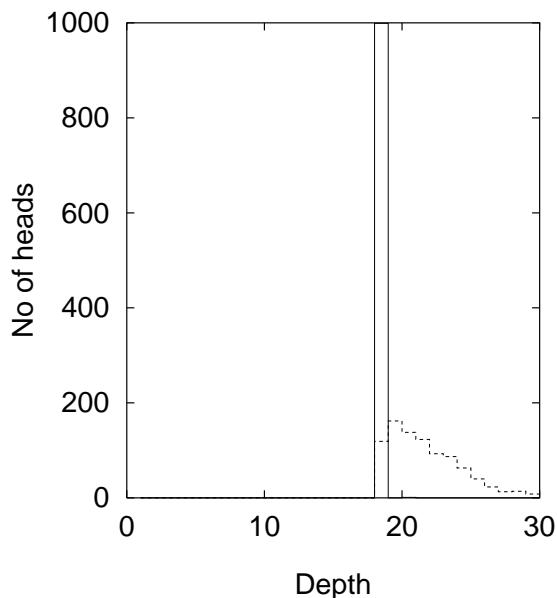


FIG. 19. Concentration profiles for heads when the number of amphiphiles is 500. Solid line is for hydrophobic spacer and broken line for hydrophilic spacer.

The conclusions drawn from averaged concentration profiles are supported by the instantaneous snapshots of the surfactants (not shown in any figure).

V. SUMMARY AND CONCLUSION:

In this paper we have developed models of both ionic and non-ionic gemini surfactants with hydrophobic spacers as well as those with hydrophilic spacers. We have investigated the morphologies of the micellar aggregates of these gemini surfactants and computed the corresponding CMCs by carrying out MC simulations.

The main features of the aggregation of gemini surfactants with *hydrophobic* spacers can be summarized as follows: (i) the micelles are far from spherical- for short spacers these are long "thread-like" and for long

spacers these are "rod-like"; (ii) the CMC varies non-monotonically with increasing spacer length; (iii) the CMC increases with the increase of the bending stiffness of the tails and spacers.

The main features of the aggregation of gemini surfactants with *hydrophilic* spacers can be summarized as follows: (i) the micelles are more or less spherical; (ii) the CMC decreases monotonically with increasing spacer length; (iii) the CMC decreases with the increase of the bending stiffness of the tails and spacers.

In contrast to the case of single chain surfactants the CMC increases with the hydrocarbon tail length for both the ionic and non-ionic gemini surfactants irrespective of whether the spacer is hydrophobic or hydrophilic. However like the case of single chain surfactants the morphologies of the ionic gemini surfactants are identical to that of the corresponding non-ionic gemini surfactants both for hydrophobic as well as hydrophilic spacer.

Therefore, we conclude that (i) the shapes of aggregates are dominantly determined by the geometric shape and size of the molecules and whether the spacer is hydrophobic or hydrophilic, whereas (ii) the variation of CMC with spacer length is strongly influenced by the ionic charge and, again, whether the spacer is hydrophobic or hydrophilic.

In the case gemini surfactants at the air-water interface for dilute regime, the cross-sectional area for single isolated gemini surfactant increases with the spacer length both for hydrophobic and hydrophilic spacer. However beyond a certain length of the spacer the cross-sectional area is larger for the hydrophobic spacer as compared

to that for hydrophilic spacer. These trends are consistent with the variation of vertical extension $\langle Z \rangle$ with spacer length; a larger value of $\langle Z \rangle$ for hydrophilic spacer as compared to the hydrophobic spacer of identical length is observed in our simulations.

For extremely high surface density of surfactants at the air-water interface we have demonstrated qualitatively the spatial organization of the gemini surfactants for both the case of hydrophobic and hydrophilic spacers.

In view of the above observations, it seems that the main effects of introducing the spacer is to impose an additional geometrical constraint on the packing of surfactant molecules and, therefore, to influence their aggregate shape and other properties.

Molecular dynamics (MD) simulations of a similar molecular model of gemini surfactants has been carried out by Karaborni et al.²¹. In their model, particles of water interact mutually via a truncated Lennard-Jones (LJ) potential with sufficiently long cut-off to incorporate both the short-range repulsion and long-range attraction. The mutual interactions between the pairs of particles belonging to the tail were also similar. But, the cut-off range of the tail-water and head-head interactions were so short that no attraction was possible. However, the chains and spacers simulated by Karaborni et al. were much smaller than those investigated in our paper here. Besides, Karaborni et al. neither investigated the CMC and its variations with lengths of the tails and spacer nor considered any model of gemini surfactants with hydrophilic spacers. One should also try to develop more efficient MD algorithms to repeat our computations with

more realistic interaction potentials on a continuum to check if any of the morphologies observed in this paper have been influenced significantly by the discrete lattice.

It would be interesting to investigate the effects of weakening of the screening (i.e., increasing the range) of the repulsive Coulomb interaction between the ionic heads on the results reported in this letter; but, such a MC study will require much larger computational resources.

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